The peculiarities of phase transitions in layered ferroelectrics-semiconductors $TlIn_{1-x}Fe_xS_2$

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February 1, 2008

Abstract

The results of differential-thermal analysis of various samples as well as dielectric measurements of solid solutions $TlIn_{1-x}Fe_x^{56,57}S_2$ are presented. It has been established that phase transitions become blurred and shift to low temperatures with increasing the concentration of defects in the layered structure. at some threshold value the structure loses layerity, the crystal becomes isotropig and the distribution of defects does homogeneous.

1 Introduction

According to data of neutron diffraction measurements [1] and x-ray investigations [2] the monoclinic modification of layered ferroelectrics -semiconductors

$TlInS_2$ undergoes a sequence of structural phase transitions with the intermediate incommensurate phase having the modulation vector $\vec{q}_{inc} = (\delta; \delta; 0.25)$, where $\delta = 0.012$.

$TlInS_2$ crystals have the space group symmetry C_{2h}^6 [2] at the high-symmetric phase ($T > 220K$). The ionic-covalent bonds in layers and ones of Van-der-Waals type between layers are competive interactions in the structure of these crystals [3]. Inproper ferroelectric phase transitions in $TlInS_2$ are intermediate between types of mixing and order-disorder with the characteristic value of Curie's constant $C \sim 10^3 K$ [4].

An analysis of experimental data by the temperature dependence of dielectric constant for various samples $TlInS_2$ with monoclinic structure shows that the $\epsilon(T)$ curves characterized for proper ferroelectrics with incommensurate phase acquire the form characteristic for inproper ferroelectrics with incommensurate phase (Fig.1, curves 1,2,3). The detailed study of results of neutron diffraction measurements [1], x-ray [2], nuclear magnetic resonance and nuclear quadrupole resonance investigations [5,6] allows to conclude that layered compounds $TlInS_2$ depending on concentration of defects in the structure have different character of phase transitions. Besides the considerable mobility of atoms in an interlayer space imparts to the structure the properties of weak glass [7].

At certain value of concentration of defects in the structure the system losing the property of layerity becomes isotropic. The range of existence of incommensurate phase and the position of Lifshits' points on the diagram of states depend on concentration of defects in the structure. For the most widespread group of samples $TlInS_2$ the dependence $\epsilon(T)$ is characterized by the evistenge of two maxima and the value of low temperature peak varies in the large range (Fig.1, curve 2) [8].

The anomaly shows itself on the dependence $\epsilon(T)$ in the range of existence of incommensurate phase at $T_{ic} \simeq 204K$ in addition to maxima at T_i and T_c for frequently occurred and detailly investigated samples $TlInS_2$. Experimental investigations show that the incommensurate phase springs up in the temperature range in which the spontaneous polarization differs from zero [9].

In seldom occurred samples $TlInS_2$ (with large concentration of defects) the dependence $\epsilon(T)$ (Fig.1, curve 1) [10] is typical for isotropic inproper ferroelectrics like Rb_2Znbr_4 [11] . In this work the results of differential-thermal analysis (DTA) of various samples $TlInS_2$ as well as dielectric measurements

of $TlIn_{1-x}Fe_x^{56,57}S_2$ are presented.

2 The Results of Differential-Thermal Analysis and Dielectric Measurements

Single crystals of $TlInS_2$ compound were grown by modificated Bridgman method at small variation of growth conditions. For dielectric measurements the samples had the form of parallelepiped with parallel edges orientated along crystallographic directions. The silver paste was used as contacts put on polished surfaces. The measurements of dielectric constant ϵ were carried out on the frequency $1kHz$ in the temperature range $100 - 300K$. The rate of temperature change was $0.1K/min$.

The results of DTA of various samples $TlInS_2$ are presented on Fig. 2. The samples with one maximum on the $\epsilon(T)$ dependence show only one endothermal effect at $1020K$ on the DTA curve stipulated by melting with the melting heat $155.75KJ/mol$. The samples $TlInS_2$ with two maxima on the $\epsilon(T)$ dependence have two endothermal effects at temperatures 920 and $1060K$ with the melting heats $80KJ/mol$ and $125KJ/mol$, respectively. Two endothermal effects at temperatures 920 and $1020K$ with the melting heats 78 and $135KJ/mol$, respectively, are detected on the DTA curve for samples displaying three maxima in the temperature dependence of dielectric constant.

The results of dielectric measurements for compounds $TlIn_{1-x}Fe_x^{56,57}S_2$, where $x = 0; 0.01; 0.1$, at both the regime of cooling and the regime of heating are presented on Fig. 3. An analysis of experimental data of temperature dependence of dielectric constant $\epsilon(T)$ allows to conclude:

-at any x the values of $\epsilon(T)$ in the regime of heating are more than in the regime of cooling;

-at any x the $\epsilon(T)$ dependence displays two maxima, and the temperature interval between them does not almost depend on temperature;

-at increasing x the temperature interval of existence of incommensurate phase shifts to low-temperature region;

-at increasing x the response of system decreases;

-at increasing x the transitions at T_i and T_c acquire the character of blurred phase transition;

-with increasing x the $\epsilon(T)$ curve loses the shape and acquires the form characterized for inproper ferroelectrics with incommensurate phase;

-substitution of Fe^{57} on Fe^{56} does not change the temperature width of existence of incommensurate phase and shifts it to high temperatures.

3 Discussions

According to data of x-ray investigations the atoms Tl in the elementary cell of crystals $TlInS_2$ occupy the general position [2]. Besides these atoms have high mobility in the interplane space [5]. Nuclear quadrupole resonance investigations indicate on the anomaly at temperature $250K$ [6,12]. Evidently, the relative displacement of atoms Tl in the elementary cell occurs at $250K$ and this deformation does not change the space group symmetry of the crystal. In addition, the deformation of the band structure of $TlInS_2$ and levels of adhesion take place. An increase of concentration of carriers decreases the temperature of transition to the incommensurate phase and increases the response of this system on the external influence. These facts explain the temperature dependence $\epsilon\,(T)$ in the high-symmetric phase. Although experimental data about details of disordering in the compounds with blurred phase transitions are absent [13], the broadening of the phase transition is general phenomenon for solid solutions and other disordered structures.

With increasing of concentration of defects in the layered structure the blurring of phase transitions at T_i and T_c and their shift to low temperatures happen. At some threshold value the layerity of structure loses and the crystal becomes isotropic and distribution of defects does homogeneous. As known, if the disordering is homogeneous, a clear phase transitions observed even in amorphous structures [14].

An increase of a depth of minimum in the temperature dependence $\epsilon\,(T)$ is the result of intensification of the constant of interaction of polarization with the amplitude of the order parameter. Consequently, with increasing x the interaction of polarization with the amplitude of the order parameter rises while it decreases with the phase. Incidentally, the incommensurate phase behaves inself as modulated one in which the soliton regime is absent. The temperature hysteresis of $\epsilon\,(T)$ connects with the temperature dependence of the band gap with accuracy to the energy of adhesive level and it connects with the inner mobility of impurities of the structure.

In the perfect layered samples $TlInS_2$ a sequence of structural phase transitions: highsymmetrical-incommensurate I-incommensurate II-commensurate phase, are sprung up.

With increasing of concentration of defects in the layered structure of $TlInS_2$ the line of Lifshits' points on the states diagram shifts and the incommensurate phase II in dielectric measurements is not observed.

With further rise of concentration of defects in the structure the compound $TlInS_2$ loses the property of layerity and the sample becomes isotropic. The temperature dependence of dielectric constant of isotropic samples at the transition from the high-symmetric phase to the incommensurate phase remains continuous, the incommensurate phase has not the minimum and behaves itself as $\epsilon \sim (T - T_c)^{-1}$. Consequently, the dependence of physical properties of $TlInS_2$ on concentration of defects is the result of existence of competing interactions in the structure.

The principal parameter determining the mechanism of melting is the energy required for the rupture of bonds in the structure [14]. That is why, only one endothermal effect shows itself in the isotropic samples of $TlInS_2$. Layered samples $TlInS_2$, having the temperature dependence with two or three maxima, show themselves two endothermal effects on the DTA curve.

The opposite isotropic effect connected with substitution of Fe^{57} on Fe^{56} in the $TlIn_{1-x}Fe_xS_2$ compounds is not the result of the rise of the tunneling frequency between two positions of equilibrium. The existence of blurred phase transition and the fact of a decrease of temperature of phase transition with a rise of concentration of defects testifies that the samples with Fe^{57} more regulated than ones with Fe^{56}.

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FIGURE CAPTIONS:

Fig.1. Temperature dependence of dielectric constant $\epsilon(T)$ of crystals $TlInS_2$ (obtained from various technologic batches) in the regime of cooling

Fig.2. The DTA curves of crystals $TlInS_2$ (obtained from various technologic batches)

Fig.3. Temperature dependence of dielectric constant of solid solutions $TlIn_{1-x}Fe_xS_2$:

curves $1, 2$ corresponds to the value $x = 0$

curves $3, 4$ - $x = 0.1$ (Fe^{56})

curve 5 - $x = 0.01$ (Fe^{57})

curves $6, 7$ - $x = 0.1$ (Fe^{57})

curves $1, 3, 5, 7$ are measured in the regime of cooling, curves $2, 4, 6$ -in the regime of heating.

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